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Magnetic and microwave absorbing properties of Co–Fe thin films plated on hollow ceramic microspheres of low density

Sung-Soo Kim[a,*], Seon-Tae Kim[a], Joon-Mo Ahn[b], Keun-Hong Kim[b]

[a] Department of Materials Engineering, Chungbuk National University, Gaesindong San 41, Cheongju 361-763, South Korea
[b] Agency for Defense Development, Yoosung P.O. Box 35, Taejon, South Korea

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Abstract

Conductive and magnetic microspheres are fabricated by plating of Co–Fe alloy thin films on hollow ceramic microspheres of low density for the application to lightweight microwave absorbers. Metal plating was carried out in a two-step electroless plating process (pre-treatment of sensitizing and subsequent plating). Uniform coating of the film with about 2 μm thickness was identified by SEM. High-frequency magnetic and microwave absorbing properties were determined in the rubber composites containing the metal-coated microspheres. Due to the conductive and ferromagnetic behavior of the Co–Fe thin films, high dielectric constant and magnetic loss can be obtained in the microwave frequencies. In particular, the magnetic loss increases with Fe content in the alloy films and its frequency dispersion can be explained by ferromagnetic resonance theory. Due to the electromagnetic properties, high absorption rate and thin matching thickness are predicted in the composite layers containing the metal-coated microspheres of low density (about 0.8 g/cc) for the electromagnetic radiation in microwave frequencies.

Keywords: Microwave absorber; Cobalt-iron thin films; Hollow microspheres; Electroless plating; Complex permeability

1. Introduction

In Recent years, microwave absorptive materials draw more attention because of its widespread applications for many electromagnetic compatibility (EMC) purposes. A number of materials have been described in the prior arts, which are capable of absorbing electromagnetic radiation. However, the conventional absorptive materials such as metal powders and ferrites are quite heavy, which restricts their usefulness in applications requiring lightweight mass [1,2]. Moreover, those materials have difficulties in increasing the permeability in GHz region because of Snoek limit for ferrites [3] or eddy current loss for magnetic metals [4].

As one of the ways to overcome these problems, the use of metal thin films coated on microspheres (or microballoons) of low density has been suggested. Gindrup [5] proposed an electromagnetic radiation absorptive composition, which comprises microballoons having a thin coating of metal (Ag) on the microsphere surface. The result has significance in providing a new technique to

*Corresponding author. Tel.: +82432612418; fax: +82432713222.
E-mail address: sskim@chungbuk.ac.kr (S.-S. Kim).

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produce lightweight absorbers in microwave frequencies. However, since the coating on microspheres is confined to only single layer of Ag (which has only conduction loss), the microwave absorption was inferior to conventional absorptive materials such as ferrite or carbonyl iron.

In resonant absorbers of quarter wavelength, zero-reflection can be obtained by access to wave impedance matching at the surface of the absorbing layer, which requires a proper combination of magnetic permeability and dielectric permittivity at a given thickness and frequency [6]. Those material parameters in high frequencies can be controlled by use of magnetic metals (permittivity control by electrical property and permeability control by magnetic property) in a single-layered microwave absorber.

The present study proposes Co–Fe alloy thin films as the coating layer on the hollow microspheres. According to the bulk magnetic properties of Co–Fe alloy [7], the crystal anisotropy field is sensitively reduced by Fe addition in Co-rich compositions by change of easy-axis of magnetization. It was expected that frequency dispersion of magnetic permeability could also be controlled by Fe content in the alloy films. The Co–Fe thin films were coated on the microspheres by electroless plating and their high-frequency properties (complex permeability and permittivity) and microwave absorbance were investigated in GHz frequencies.

2. Experimental procedure

Commercially available hollow microspheres were obtained from PQ Cooperation (Valley Forge, PA, USA). The microspheres have a hollow ceramic (silicate) shell of a few μm thickness and thus having a low density of 0.2 g/cc. Metals (Co and Co–Fe alloy) plating was carried out in a two-step operation in which the surface of microspheres is first sensitized by treatment with salts of metal ($PdCl_2$–$SnCl_2$), followed by chemically reducing the salts of metals ($CoSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$) using a mild reducing agent of $NaPH_2O_2 \cdot H_2O$.

Seven grams of microspheres were placed in a funnel with a catalyst solution of $PdCl_2$ (0.01 mol/l), $SnCl_2 \cdot 2H_2O$ (0.01 mol/l) and HCl (100 mol/l). This mixture was shaken at 50°C for 30 min. The microspheres were then washed with distilled water, gravity filtered, and air dried at 60°C.

1 g of the pre-treated microspheres was placed in 500 ml of plating solution containing 8.0 g of salt of cobalt ($CoSO_4 \cdot 7H_2O$) and salt of iron ($FeSO_4 \cdot 7H_2O$), 8.5 g of reducing agent ($NaPH_2O_2 \cdot H_2O$), 57.5 g of complexing agent ($Na_2C_2H_4O_6 \cdot H_2O$) and 10 ml of pH modifier (NH_4OH), and the mixture was tumbled at 80°C for 1 h. The mol ratio of $FeSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 7H_2O$ was controlled in the range that the Fe content in the film is 5–10 at%. During plating, pH was controlled to be 8.5. The metal-coated microspheres were gravity filtered, washed with distilled water and air dried at 60°C. The batch was repeated three times for the complete coating of the metal film.

Uniformity of coating layer was identified by two methods. One is by measurement of apparent electrical resistance of powder compacts and the other is by direct observation using SEM. Apparent resistance was measured in a compact of 0.05 g metal-coated microspheres pressed slightly in an insulated cylinder mold of 10 mm inner diameter.

The complex permeability and permittivity was measured in the composite specimens of the metal-coated microspheres dispersed silicone rubber matrix. The mixing ratio of particles to rubber was 1:1 by weight (5.5:4.5 in volume ratio). Toroid sample (inner diameter of 3 mm, outer diameter of 7 mm, and thickness of about 2 mm) was inserted in a standard coaxial sample holder (APC-7 beadless air line), and reflection coefficient (S_{11} parameter) and transmission coefficient (S_{21} parameter) were measured by using HP8722D network analyzer. Frequency range of the measurement was 1–18 GHz. The complex permittivity and permeability was calculated from the S_{11} and S_{21} parameters. Reflection loss was determined by measuring the S_{11} parameter after rear face of sample was terminated by metal.

3. Results and discussion

Fig. 1 shows the SEM observation of the non-coated silica microspheres and their surface structure. Spherical particles with an average diameter of about 70 μm were observed. No grain boundary observed in the surface structure indicates that the silica shell is composed of glassy phase.

Fig. 2 shows the microstructure of the microspheres coated with Co films by electroless plating. Uniform coating of Co film and its smooth surface morphology can be observed. Some small irregular particles are considered to be free Co precipitates formed during plating. But their amount is quite small. Low value of apparent electrical resistance (about 0.1 Ω) measured in the powder compacts of the Co-coated microspheres also provides an indirect evidence of complete coating.

Starting with 1.0 g non-coated microspheres, the weight gain was measured to be 3.5 g after plating. Due to this weight gain, the density was also increased from 0.2 g/cc (non-coated microspheres) to 0.8 g/cc (after plating). The thickness of film roughly estimated from the weight gain and theoretical density was about 2 μm, which was also identified by SEM observation.

Fig. 3 shows the complex permeability ($\mu_r = \mu_r' - j\mu_r''$) and permittivity ($\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$) determined in the composite of non-coated microspheres and silicone rubber matrix of which weight ratio was 1:1. Because of non-magnetic property of the constituent materials, the complex permeability was determined to be $\mu_r' = 1$ and $\mu_r'' = 0$. Small value of dielectric constant ($\varepsilon_r' = 2.6$) and negligibly small dielectric loss ($\varepsilon_r'' \cong 0$) was estimated.

The Co film plated on the microspheres increases both magnetic permeability and dielectric permittivity as shown in Fig. 4. In particular, the increase of magnetic loss (μ_r'') and dielectric constant (ε_r') is evident. Slightly increasing function of μ_r'' (from zero at 1 GHz to 0.26 at 18 GHz) and decreasing function of μ_r' (from 1.2 at 2 GHz to 0.8 at 18 GHz) with frequency is observed. Due to high anisotropy field of Co thin film, the magnetic loss appears in the high frequencies.

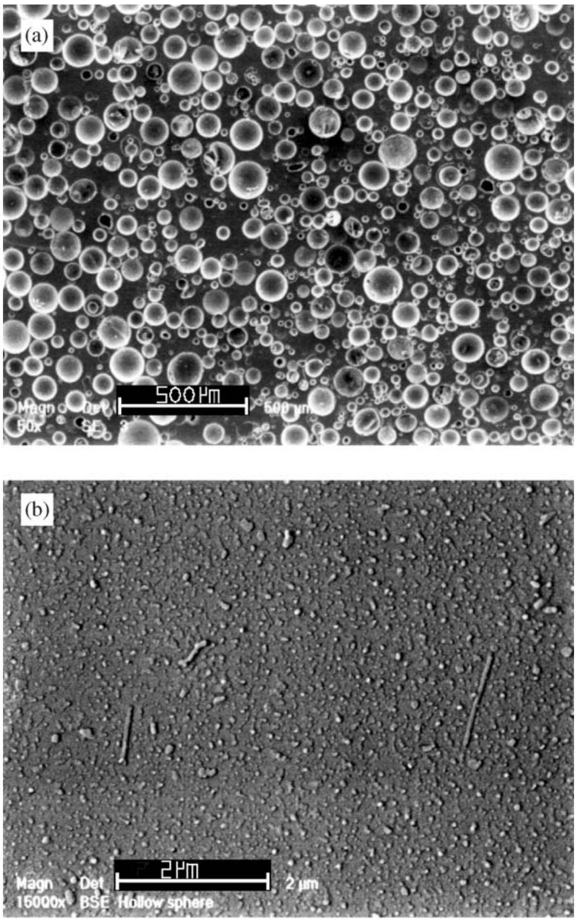


Fig. 1. SEM morphology of (a) hollow microspheres and (b) its surface structure.

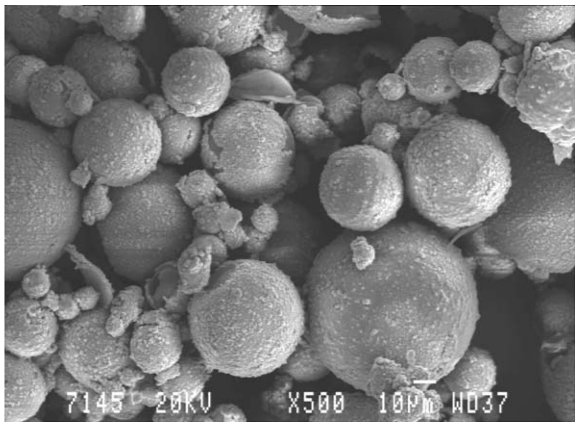


Fig. 2. SEM morphology of Co-coated microspheres.

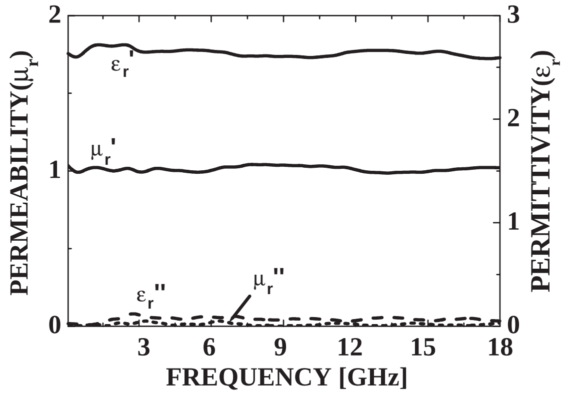


Fig. 3. Material parameters of non-coated microspheres dispersed in rubber matrix.

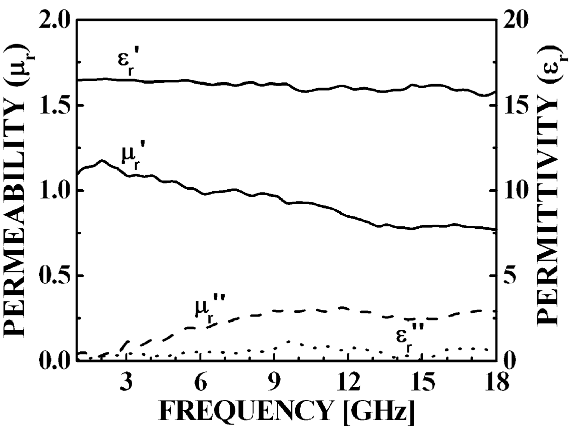


Fig. 4. Material parameters of Co-coated microspheres dispersed in rubber matrix.

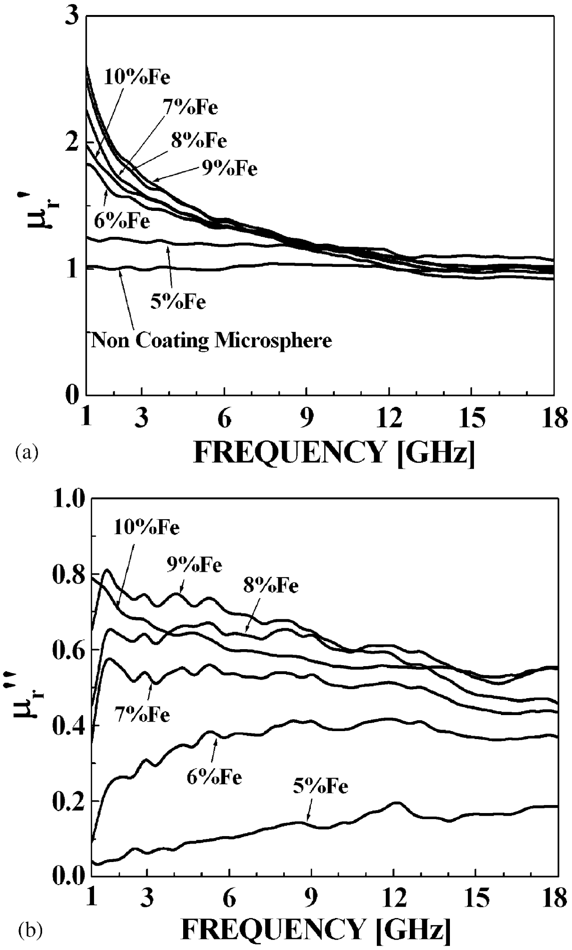


Fig. 5. Complex permeability of composites containing microspheres coated with Co–Fe thin films: (a) μ_r' and (b) μ_r''.

High value of dielectric constant ($\varepsilon_r' \cong 17$) is attributed to metallic behavior of Co thin film. The space charge polarization between adjacent conductive particles (separated by insulating rubber matrix) gives rise to a high value of dielectric constant. However, the conduction loss (represented by ε_r'') was observed to be small (loss tangent less than 0.1).

Fig. 5 shows the frequency dispersion of complex permeability of Co–Fe films with variation of Fe content (5–10 at%). The coating composition was controlled by the mole ratio of metal sources in the plating solution under the assumption that the film has the same composition as that of plating solution. The value of μ_r' increases with Fe content in the lower frequency region below 9 GHz (Fig. 5(a)). For instance, at 1 GHz μ_r' increases from 1.2 (5 at% Fe) to 2.6 (9 at% Fe). Magnetic loss (μ_r'') also increases with the Fe content and dispersion peak of μ_r'' moves to lower frequency (from 18 GHz for 5 at% Fe film to 1.2 GHz for 9 at% Fe film) as shown in Fig. 5(b). For 10 at% Fe film, the μ_r'' peak frequency is considered to be lower than 1 GHz. If the resonance frequency is below 1 GHz for the 10% Fe coating, both real and imaginary parts of permeability can be smaller than that of 8 and 9 at% Fe films in the frequencies above 1 GHz as shown in Fig. 5. The similar frequency spectrum of permeability can be found in $Co_{\delta}Zn_{2-\delta}Z$ hexagonal ferrites where the higher the initial permeability (the lower the resonance frequency), the smaller the value of permeability (both real and imaginary) in the high frequencies [3].

Fig. 6 shows the hysteresis loops determined in the microspheres coated with Co and Co-10 at% Fe films. The saturation magnetization M_s increases from 54 emu/g (Co film) to 134 emu/g (Co-10 at% Fe film), which is due to higher magnetic moment of Fe atom. On the while, the coercive force H_c decreases from 450 Oe (Co) to 110 Oe (Co-10 at% Fe). According to the bulk magnetic properties of Co–Fe alloy [7], the magnetocrystalline anisotropy is changed from uniaxial *c*-axis to in-plane of HCP at 1.0 at% Fe, and then to cubic anisotropy of FCC at 5.2 at% Fe. Fe substitution in Co lattices in the composition range reduces the crystal anisotropy field and, therefore, lower H_c was predicted in the microspheres coated with Co–Fe films. The similar behavior of crystalline anisotropy was observed in M-type hexaferrites, where easy axis is changed from c-axis to in-plane by substitution of Ti–Co ions for Fe sites [8].

According to the ferromagnetic resonance theory [9], the resonance frequency f_r is proportional to the anisotropy field H_A as expressed by the equation,

$$f_r = \frac{\gamma}{2\pi} H_A, \quad (1)$$

where γ is gyromagnetic ratio. For the films coated on the spherical particles, shape anisotropy field can be negligible. H_A is then crystal anisotropy field, which is given by

$$H_A = \frac{2K}{M_S}, \quad (2)$$

where K is crystalline anisotropy constant. Since the coercive force is, in general, proportional to the anisotropy field, the resonance frequency increases with the coercive force. The result of permeability dispersion is quite well consistent with the ferromagnetic resonance theory.

The complex permittivity is insensitive to Fe content as shown in Fig. 7. Slightly different

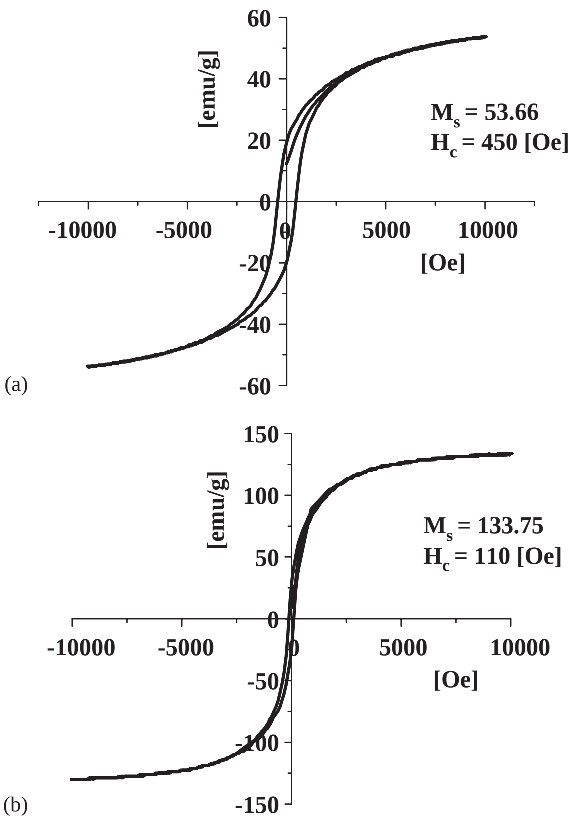


Fig. 6. Hysteresis loops determined in the microspheres coated with (a) Co and (b) Co-10% Fe thin films.

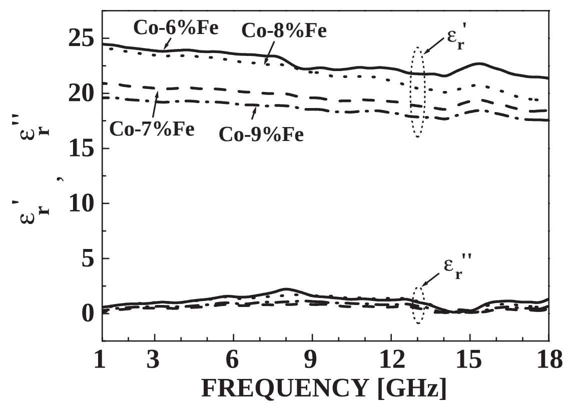


Fig. 7. Complex permittivity of rubber composites containing microspheres coated with Co–Fe thin films.

values of $\varepsilon_r' = 20-24$ and small value of ε_r'' (loss tangent less than 0.1) was determined. The electrical conductivity does not change considerably with Fe content in the films, which results in not so different values of dielectric constant.

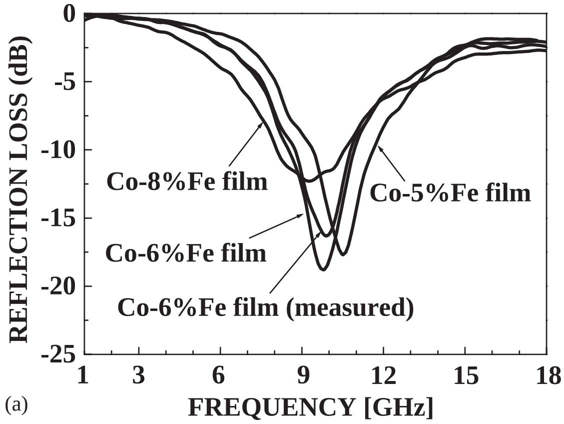
For the composite layer (of metal-coated microspheres and rubber matrix) terminated by metal plate, the input impedance Z_{in} at the surface is given by

$$Z_{in} = Z_0\sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[\frac{j2\pi d}{\lambda}\sqrt{\varepsilon_r\mu_r}\right], \tag{3}$$

where Z_0 is wave impedance of free space (376.7 Ω), λ is wavelength in free space, and d is thickness of composite layer. Since the reflection coefficient Γ is proportional to the difference between Z_{in} and Z_0 as expressed in Eq. (4), the reflection loss can be calculated from the measured material parameters (μ_r and ε_r) as a function of frequency and thickness.

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0}. \tag{4}$$

Fig. 8 shows the reflection loss determined in the rubber composites containing the microspheres coated with Co–Fe films. At the thickness of 1.5 mm, the microwave absorption (more than 10 dB) occurs in the X-band frequencies (8–12 GHz) as shown in Fig. 8(a). The measured value of reflection loss is also given for the sample of 6 at% Fe coating. There is a small difference in maximum attenuation between theoretical (−18 dB: 98% power absorption) and experimental result (−16 dB: 97% power absorption). However, the difference is quite small in power absorption. By increasing the thickness to 2.0 mm, the absorption band moves to the lower C-band frequencies (4–8 GHz) as shown in Fig. 8(b). The maximum absorption (more than 20 dB) was predicted at the composition of 6 at% Fe. A slight difference in microwave absorbance is observed by the variation of film composition. The absorption band moves slightly to lower frequency with increase of Fe content in the films, which might be due to higher magnetic loss as shown in Fig. 5(b).



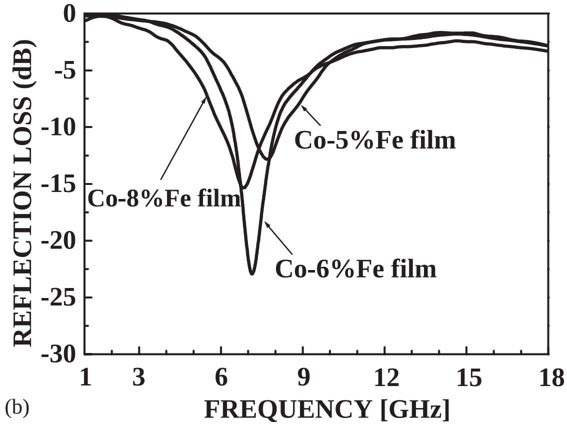


Fig. 8. Reflection loss determined in the rubber composites containing the microspheres coated with Co–Fe thin films: (a) $d = 1.5$ mm and (b) $d = 2$ mm.

It has been reported that for the previously developed X-band absorbers composed of ferrite particles and rubber matrix, the typical value of thickness is about 3 mm [10]. The predicted matching thickness of this study is quite small compared with the conventional ferrite composite absorber, and the result is attributed to the higher magnetic loss and dielectric constant of the Co–Fe films. Moreover, the density of the metal-coated microspheres is very low (0.8 g/cc) as compared with ferrites (5.7 g/cc). The proposed conductive and magnetic microspheres coated with Co–Fe films has advantages in reducing both mass and thickness when used as the absorbent fillers of microwave absorbers.

4. Conclusions

Lightweight and thin microwave absorbers could be demonstrated by using the hollow ceramic microspheres coated with Co–Fe thin films as the absorbent fillers in rubber matrix. Highly conductive and magnetic microspheres of low density (about 0.8 g/cc) could be prepared by plating the Co–Fe thin films on the microspheres. Due to metallic and ferromagnetic behavior of the Co–Fe films, high dielectric constant and magnetic loss could be obtained in microwave frequencies. It was found that the higher the Fe content in the alloy films, the higher the magnetic loss (μ_r'') and the lower the dispersion peak frequency of μ_r''. The result could be well explained by ferromagnetic resonance theory. Due to these electromagnetic properties, high absorption rates for electromagnetic radiation and thin matching thickness were predicted in the rubber composites containing the metal-coated microspheres. Reflection loss less than -20 dB were predicted in X-band frequencies with a thickness of 1.5 mm. The proposed absorber is well advanced in both mass and thickness in comparison with the conventional ferrite absorber.

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